Synopsis

Thermal barrier coating systems (TBC's) employed in the high pressure turbine section of a modern aero-turbine engine serve as an example of constrained material systems used for engineering applications. TBC's today are constituted of a Ni-based superalloy substrate coated with a bond coat for providing oxidation protection at high temperatures and a ceramic top coat made of Yttria stabilized Zirconia. When exposed to the oxidative environment in the aero-turbine engine the bond coat aids in the formation of a thin layer of thermally grown oxide (TGO) sandwiched between the bond coat and the ceramic top coat. The entire TBC system undergoes thermo-mechanical fatigue in service. Failure initiates due to edge delamination and large scale buckling of the TGO leading to spallation of the ceramic top coat [1]. The thin layer of bond coat, which is typically a Nickel aluminide or NiCoCrAlY based coating, could also be responsible for initiating failure in the TBC system. These bond coat systems alleviates and redistributes the in-plane compressive residual stresses of the TGO by undergoing viscoplastic creep at high temperature. In service, the bond coat system accommodates stresses that develop due to thermo-mechanical mismatch from both the underlying substrate and the ceramic top coat as the oxide layer thickens. Since the fracture toughness of the ceramic top coat as well as the interface with the thermally grown oxide is inherently weak due to its brittle constitution and porous nature, the actual protective function is played by the bond coat. There are a wide range of studies on the mechanical response of the composite TBC system and studies at the length scales involving the bond coat are lacking. Knowledge in this regard gains more significance in systems which possess only the bond coat without the ceramic topcoat like land based gas turbines.

The work presented in this thesis has been motivated mainly by previous studies on the mechanical property evaluation of commercial platinum modified nickel aluminide bond coats on superalloy substrates. These diffusion aluminide bond coats possess an internal length scale of microstructural heterogeneity that extends up to ~10-15μm, depending on the local micro-chemistry and microstructure. Recently Jaya et.al [2] suggested the

clamped beam geometry as an ideal geometry suited for probing the fracture toughness of these graded coatings at these length scales of interest. Clamped beams fabricated from different zones within platinum nickel aluminide bond coats were loaded to fracture using a wedge shaped indenter tip using a nano-indentation system. The fracture toughness was computed from the fracture loads using an extended finite element formulation as analytical stress intensity factor solutions are not available for a clamped beam geometry. The variations in the fracture toughness values across the thickness of the bond coat were studied as a function of platinum concentration and micro mechanisms associated with the observed toughening were analyzed to be a combination of materials microstructure (crack bridging and kinking observed due to interaction with precipitates) as well as size effects [3].

In this study the versatility of the clamped beam geometry, in terms of exploring local properties of thin graded coatings, is extended further by using it to study the cyclic behavior of different zones within platinum nickel aluminide bond coats. Notched clamped beam structures fabricated from distinct microstructural zones of the coating are subjected to cyclic loading using the nano-indentation system. The stiffness of the beam is used as an indicator to mark failure and is continuously monitored during the test. A systematic procedure is established herein to quantitatively report a methodical approach to provide such signatures for different zones within the coating. The thesis reads in the following way:

Chapter 1 highlights the importance of small scale testing methodologies for investigating the structural integrity of functionally and structurally graded components and qualitatively differentiates between small scale and bulk scale tests. Reasons for evaluating the mechanical properties of bond coats have been stated and the clamped beam geometry that has been adopted for fracture toughness testing of platinum aluminide bond coats has been introduced.

Chapter 2 provides the general background and literature on platinum aluminide bond coats and thermal barrier coating (TBCs) systems that forms the backbone for this study. The complex failure modes of thermal barrier coating systems have been discussed with emphasis on bond coat driven failure in such systems. The pack aluminization process was used for the coatings in the present study. The general details of the pack aluminization process and typical microstructural variations accompanying different heat treatment schedules have been presented. The mechanical properties of nickel aluminide based bond coat systems have been evaluated by various groups and most of these studies have been carried out on aluminide coated superalloy substrates. The presence of substrate poses issues in the interpretation of the mechanical data obtained because there could be interactions between the substrate and the coating during deformation and thus some groups have been involved with the testing of free standing coatings. The results obtained from such tests have been reviewed. The fracture stability of the clamped beam fracture geometry introduced by Jaya et.al has been discussed. Fracture toughness values obtained from different zones of the platinum nickel aluminide system and its correlations to local microstructure and micro-chemistry have been highlighted. The base matrix for the bond coat is β-NiAl which is known for its anisotropic elastic response. The anisotropic behaviour mainly arises from the strong Ni-d Al-p hybridization along the [111] direction which is absent along the [100] direction which results in stronger bonding along the [111] direction. This elastic anisotropy produces highly orientation specific response in these systems with specific cleavage planes being preferred for fracture. Some of the fracture experiments performed on single crystalline NiAl to investigate this anisotropic response have been reviewed. Also, fatigue crack growth in such brittle intermetallic systems is notably different from fatigue in ductile metals. Internal dislocation substructures that develop in these ordered alloys after cycling are different from ductile metals like copper and iron. The formation of persistent slip band (PSB) was observed in fatigued NiAl samples and these PSBs have long dislocation dipoles knitted at intermediate points. Some of the room temperature fatigue mechanisms operatives in single & poly-crystalline NiAl have been reviewed which motivated the current study on the cyclic response of platinum aluminide bond coats.

Chapter 3 describes the experimental methods and necessary calibrations adopted in the present study. The pack aluminization procedure adopted for the coatings used in the present study have been discussed with emphasis on the effect of platinum on the microstructural evolution of the coatings. The current method employed for cyclic testing of clamped beams involves extensive machining using the focused ion beam (FIB) microscope. The FIB was also used for extracting electron transparent foils from the tested regions of the bond coat post in-situ testing. Although, these are fairly common techniques employed by the small scale testing community the procedure has been described vividly herein for the sake of completeness. Basic characterization techniques to probe the micro-structure and the micro-chemistry of these clamped beams have also been discussed.

The depth resolution of the nano-indentation system has been extended to perform small scale bending experiments on these clamped beam structures. The unloading stiffness of the beam is used as an indicator to mark failure and the stiffness is continuously monitored during the test. The measured stiffness is the combined stiffness of the loading frame and the stiffness of the beam. Thus, calibrating the stiffness of the loading frame and the transducer is a crucial step to recover the stiffness of the clamped beam as a function of time. The cyclic experiments have been performed both ex-situ (i.e. without simultaneous viewing of the crack tip using a commercial nano-indentation system) and in-situ (pico-indentation facility interfaced with an SEM) with the latter allowing for simultaneous viewing of the crack mouth opening displacement (COD) as the fatigue cycling progresses. Such correlations between crack opening displacements and the stiffness of the beam provide useful signatures that mark crack initiation in such structures, a critical value for the opening displacement after which crack pop-in occurs.

Chapter 4 presents the important results from various tests performed on these coatings. The ex-situ testing results are presented for beams tested from two different zones in the 5PtAl coating and the top zone of the plain aluminide coating (0PtAl). These preliminary studies show that there is a characteristic change in stiffness before a crack pop-in event occurs and different regions within the coating show different stiffening characteristics.

Beams tested from different zones of the 5PtAl coating have shown that the platinum rich zone containing ζ-$PtAl_2$ precipitates cyclically strengthen as the deformation of the matrix is accommodated by the softer precipitates. We also observe that some characteristic amount of strain build up occurs in front of the notch tip as it blunts under cyclic deformation before a crack pop-in occurs. Zone within the 5PtAl coating containing brittle W-based precipitates undergo cyclic softening mainly due to micro-cracking, which can either be intergranular or at the matrix precipitate interface. This brings out the importance of K/μ (Bulk modulus/ shear modulus) or the Pugh criteria to determine whether a particular phase exhibits ductile/brittle behaviour and its influence on the cyclic deformation characteristics.

In contrast to the above, plain aluminide coatings have a higher porosity and lower initiation toughness towards the top zone which results in cyclic softening as cyclic damage gets localized to the pores. Thus Pt addition to the bond coat enhances the cyclic deformation resistance of the coating, thus improving its structural integrity.

Such localized information from different regions of a graded structure can be used for computational fatigue life predictions and for tailoring improved bond coats both micro structurally and chemically.

Chapter 5 is based on the finite element based solutions that complement the experimental data obtained from cyclic tests and provide insight into the mechanics that precedes cyclic crack initiation in such small scale tests. Since stiffness is the defining parameter in the present experimental method that correlates cyclic damage and crack initiation from the notch root, it becomes important to demarcate factors that affect its values. Geometrical parameters such as offsets in indenter contact positions have been considered first. These studies show that longer beams are less susceptible to lateral offset (0-5μm from the center of the beam) based variations in stiffness and this provides an upper bound on the length of the beam tested. Similarly, it has been validated that angular offsets of less than 5°, result in minimal variation in the observed base values of stiffness.

Since small scale yielding conditions prevail at the notch tip, and under the influence of cyclic loads micro-plastic deformation precedes crack pop-in event, the gradual stiffening/ softening of the clamped beam structures under cyclic loads can be attributed to local flow stress changes that arise from local changes in the micro-structure surrounding the notch tip, as this is where the stress concentration is highest. Under cyclic loads, as the flow stress of the material changes, the loads required to reach the same displacement as in the previous cycle, increase/decrease depending on whether the beam hardens/ softens under cyclic loads and consequently manifests itself as changes in the measured stiffness of the beam. The evolution of flow stress under the influence of cyclic loads is a localized effect that is restricted to the zone in the vicinity of the notch tip. The region surrounding the notch tip sees a compressive residual stress field owing to the mismatch in strains between the plastically deformed region and the elastic region surrounding this. The compressive residual stress field is balanced by a tensile residual stress field ahead of this region and its extent decreases with local stiffening near the notch tip. Such a mismatch in local flow fields leads to the accumulation of residual stresses upon unloading which in turn drives the mechanics of crack propagation. A graded flow stress model has been proposed in this study with linearly varying flow stress profile close to the notch tip. Such local gradation in flow stress properties provides us with an estimate of how the shape of the plastic zone evolves under cyclic stiffening and softening conditions. It also provides an estimate of the required flow stress changes that explain the experimentally observed changes in the stiffness.

Chapter 6 delves deeper into the zone-specific micro-mechanisms underlying fatigue fracture in bond coats. The inability to directly view the crack tip during the ex-situ test limits the overall conclusions that can be drawn from the test. In such a scenario, in-situ testing using the SEM as an interface, bridges the much needed gap and provides the missing information on the measurement of the full field displacements surrounding the notch tip. A detailed in-situ testing procedure was set up accordingly to correlate the local crack opening displacement field to the stiffness of the beam. In addition to this, electron transparent foils were extracted from both the front and back face of the beam to study the local microstructural details accompanying fatigue fracture in these structures. The local chemistry of the precipitates and the stoichiometry of the β-(Pt,Ni)Al matrix from different zones were mapped using the super-X quad-EDS detector present in TITAN transmission electron microscope.

For beams rich in W-based precipitates a gradual drop in the stiffness values was observed with sharp drops at the beginning of each new set of loading. This is accompanied by a corresponding jump of ~5-10nm in the crack opening displacement values at the beginning of each new set. The intermittent unloading process induces compressive residual stress fields surrounding the notch tip and at the beginning of each new set of loading these tractions are relieved with possible micro-cracking within the volume of the beam.

For the beams fabricated 30μm from the top zone, multiple instances of cracking within the beam were observed with corresponding increase in the crack opening displacement values. As further cycling is carried out on the sharp fatigue crack, closure effects become more prominent. There are intermediate segments following the stiffness drops wherein the stiffness gradually increases. This is due to closure tractions that accumulate around the crack tip surface due to cycling. The stiffness of the beam increases to some critical level as these closure tractions build up following which there is another stable crack extension event. The FIB lift out procedure for extracting electron transparent foils from the front and back face of the beam reveals that the morphology of the crack is quite different for the front and back faces of the beam. The crack initiation direction for the front and back faces differ by ~15.6° though the latter half of this crack is parallel to the direction of crack seen on the back face. This points towards the 3-dimensional nature of cracking across the width of the beam and can be associated with the micro-structural differences across the width of the coating. This discontinuity in the initiation direction requires twisting of the crack front across the width of the beam. The crack gets segmented into partial fronts across the width linked by cleavage steps and such configurations are more likely to occur in crystals with strong cleavage tendencies [4]. Such cleavage steps have been observed for the back face of the beam in the electron microscopy based investigations post testing. Crack wake zone shielding mechanisms such as crack tip dislocation shielding and crack deflection and meandering based mechanisms cause extrinsic toughening in the beams fabricated 30μm from the top zone, while for the top zone beams the extrinsic toughening is derived primarily from micro-cracking. Similarly, the interaction of the crack front with the second phase precipitates induces crack path deflection thus contributing to the extrinsic crack wake toughening mechanisms.

Finally, chapter 7 gives the closure and important conclusions from the present work. It summarizes the key testing results obtained from this study and highlights the proposed mechanisms that accompany cyclic failure in these graded coatings. Some new techniques and geometries to probe the high cycle fatigue behavior of such graded coatings using laser Doppler vibrometry have also been proposed. The last part of the chapter deals with future implications of the results found and some open threads and challenges left over from this study that are yet to be dealt with.